

Attachment A - 7 pages

Leszek A. Utracki

POLYMER ALLOYS AND BLENDS

Thermodynamics and Rheology

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3.8 Steady State Shear Flow 213

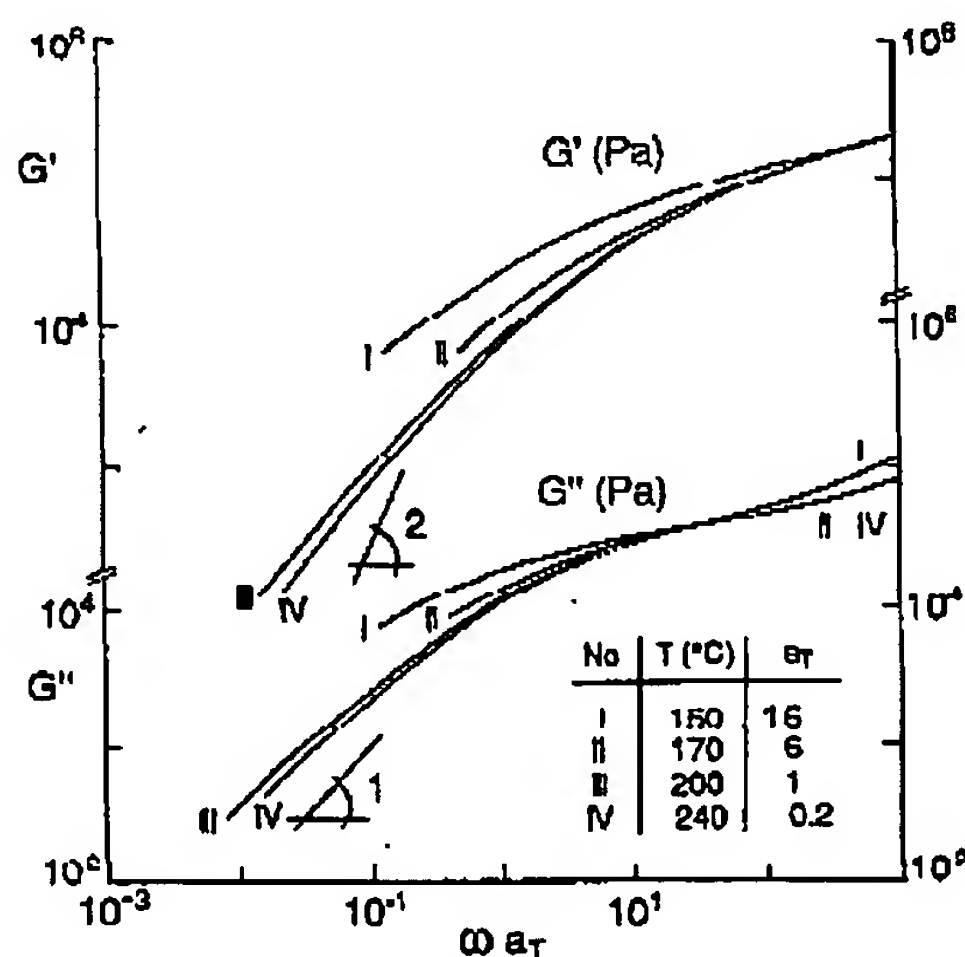


Fig. 3.47 Time-temperature superposition of shear moduli for immiscible blend of polystyrene with 33 wt% low density polyethylene (Utracki and Sammut, 1988).

Due to the diversity of morphology and rheological responses observed for immiscible blends any attempt at generalization must be viewed with suspicion. Nevertheless, on the basis of the available evidence it seems that the main condition for validity of time-temperature superposition principle, i. e. for relative stability of morphology in the full range of σ_{12} and T, are good interphase interactions, either inherent or generated by a compatibilizer. Examples of the first type are the above mentioned ABS and ASA polymeric systems.

The blends of polyethyleneterephthalate/polyamide-6,6 can serve as an example of the second type (Utracki et al., 1981, 1982; Utracki and Bata, 1983). In spite of their immiscibility and coarse, dispersed morphology (PA-6,6 content did not exceed 35 wt%) apparently the ester-amide interactions were sufficiently strong to generate consistent responses from the dynamic and steady state shearing, as well as the time-temperature superposition within the full temperature range: $245 \leq T \leq 300$ °C (the lower limit was established by the PET "softening point", the upper by the thermal decomposition). Presence of the specific interactions between ester and amide groups could also be deduced from the miscibility of systems containing about 5 wt% of PA-6,6.

The capillary flow of polyethyleneterephthalate/polyamide-6 at 275 °C was studied by Dimov and Savov (1980). The authors reported that up to the phase inversion at $w \approx 40$ wt% PA-6 the effective viscosity of blends was Newtonian for $\sigma_{12} \leq 100$ kPa. This observation finds support in the previously cited work on PET/PA-6,6 (Utracki et al., 1982).

Blends of PET with either PA-6 or with PA-6,6 both showed NDB behavior in the dependence of η (or Ψ_1) on composition. However, the depth of the negative deviation from the log-additivity rule was found to be nearly independent of the shear stress. By contrast, the NDB character in the η vs. ϕ plot for antagonistically immiscible blends such as: polypropylene/polyamide-6, PP/PA-6, (Yakovlev et al., 1984) polyoxymethylene/poly(ethylene-co-vinylacetate), POM/EVAc, (Rezanova and Tsebrenko, 1981), polyoxymethylene/polystyrene, POM/PS, (Romankevich et al., 1983) and others, significantly deepens with σ_{12} . This type of dependency is predicted by the interlayer slip model, Equation (3.166).

became more important

as were investigated in the shrinkage effect. For the oil bath at 180 °C n was defined as:

$$(3.212)$$

time t , respectively. For the shrinkage (due to residual cylinder into a sphere, the

$$(3.213)$$

respectively. Eq (3.213) initial aspect ratio, $p = L/d$. of a relative magnitude of $(\infty) \approx 3$ for 50/50 blend. interfacial interaction results swell.

of polypropylene/low density

perature (Dumoulin et al., first paper a good correlation reported for 50/50 blends in block copolymer (EP). J_{12} plot (Pe is the Bagley of the die diameter, i.e. without any sign of either of G_1 vs. ω_1 was linear, in was an observation that high initial modulus and

In the second more detailed analysis, (Dumoulin et al., 1986; Dumoulin, 1988) PP was blended with two LLDPE's, one having lower the other higher η_0 than that of PP. For both systems η_0 vs. ϕ plot indicated a local minimum for 95 wt% of PP. The plot of η_{0M} vs. η_0 (see Eq (3.209)) was similar to that observed for LLDPE blends (Utracki and Schlund, 1987). The dynamic viscosity, η' vs. ω , was well described by relation (3.62). Consequently the parameters of reduced frequency relaxation spectrum (\bar{H}_G, ω_{max}) were determined, from which the limits of miscibility were estimated.

3.7.3 Other Polyolefin Blends

Addition of a small amount of polyolefin improves the processability and impact properties of engineering resins (Utracki, 1987a, b). The optimum performance is usually reached at 2 to 4 wt% level although in patent literature, up to 20 wt% is frequently claimed (Rosengquist, 1982). Polyolefins have also been used to "extend" the performance of more expensive polymers (Sadova et al., 1977; Danesi and Porter, 1978; Akhtar et al., 1987). However, of particular interest are blends in which polyolefin is the major component, modified by addition of another more expensive resin.

To this category belong the polyolefin blends with enhanced barrier properties. In particular addition of poly(ethylene-co-vinylalcohol), polyamides, polyvinylchloride or polyvinylidene chloride is well known in the industry. These blends are immiscible, although a degree of compatibilization is required. The immiscibility is precisely the reason for selecting the ingredients; if the blends were miscible only additive permeability could be expected. Since they are immiscible, the flow imposed morphology may generate overlapping lamellae creating surprisingly high barrier properties. This principle led to the development of proprietary DuPont technology where the custom tailored mixture of a polyamide with usually ionomeric compatibilizer is added to a polyolefin resin, blended and then blow molded into bottles or drums with high barrier properties. It is interesting to note that here not so much a product but rather the rheological/engineering know-how is being marketed. Depending on the customer's resin, processing equipment and product requirements a different mixture can be formulated and introduced at different concentration level (usually up to 20 wt%). Biaxial stretching of polyamide drops, dispersed in the polyolefin matrix and bound to it by appropriate compatibilizer is responsible for creating a multilayer overlapping lamellae, significantly reducing the oxygen and/or solvent permeability. The size of polyamide drops and the resulting lamellae thickness can be controlled by the amount of compatibilizer (Willis and Favis, 1988).

Permeability is a product of solubility of the penetrant and its diffusion through the barrier material; reduction of solubility or increase of the diffusion path (tortuosity) caused by the lamellar blend structure can decrease permeability. The semi-crystalline nature of both polyethylenes and polyamides also affects the barrier properties; the best pair was found to be the high density polyethylene, HDPE, blended with poly-ε-caprolactam, PA-6 (Kamal et al., 1984). The flow behavior and the flow-imposed morphologies in the HDPE/PA-6 system were studied by Dumoulin et al. (1985) and by Utracki et al. (1986). In these works compatibilizer was not used. The initial excellent superposition of dynamic and capillary flow data obtained for HDPE disappeared upon addition of PA-6. The dynamic data were highly reproducible and measurements at $T = 150$ to 250 °C could be superimposed on a time-temperature master curve. However, since $T_m(\text{PA-6}) = 219$ °C, the a_T versus T plot did not follow any simple relation. Scanning electron micrography demonstrated that HDPE/PA-6 sample morphology was not affected by a low strain dynamic test.

In capillary flow the relative viscosity at 150 °C increased with PA-6 concentration according to Eq (3.95) whereas at 250 °C it decreased following the interlayer slip relation

172 3 Rheology of Polymer Alloys and Blends

where G_i is the shear stress relaxation modulus of blend components (Tseng et al., 1985). For two-component mixtures, assuming a single exponential form of $G(t)$, integration of Eq (3.146) gives:

$$\eta = \phi_1^2 \eta_1 + \phi_2^2 \eta_2 + 4F(G) \phi_1 \phi_2 \quad (3.147)$$

where, in the absence of specific interactions:

$$F(G) = (G_1^0 G_2^0)^{1/2} \eta_1 \eta_2 / (G_1^0 \eta_2 + G_2^0 \eta_1) \quad (3.148)$$

with G^0 the plateau modulus. Equation (3.146) is general and Wu's concept of entanglement variation with specific interactions can be easily incorporated into it. Since $F(G) \approx 0$, Eq (3.147) predicts a small NDB effect at $F(G) \rightarrow 0$.

As shown in Table 3.5 the log-additivity of η_0 vs. ϕ functions were reported for: polyvinylchloride/chlorinated polyvinylchloride (Lehr, 1986), polycarbonate/tetramethyl-Bis-A-polycarbonate (Belaribi et al., 1986), blends of two linear low density polyethylenes (Irracki and Schlund, 1987), etc. In these systems, the chemical and physical character of ingredients was similar.

TABLE 3.5 Examples of Polymer Alloys and Blends Showing Positive, Negative and Mixed Deviation from the Log-Additivity Rule. The Classification is Based on Viscosity vs. Composition Behavior, Where Viscosity was Taken at the Lowest Constant Stress.

No.	Blend	Ref.
I Positive Deviating Blends (PDB)		
I A Miscible Blends		
1.	Poly(2,6-dimethylphenyleneether)/polystyrene	1
2.	Polybutadiene fractions	2
3.	Polydimethylsiloxane fractions	3, 4
4.	Polystyrene fractions	4
5.	Polymethylmethacrylate fractions	4
6.	Linear low density polyethylenes blends	5
7.	Polyisoprene/polyvinylethylene	6
I B Immiscible Blends		
8.	High density polyethylene/poly(ethylene-co-vinylacetate)	7
9.	High density polyethylene/low density polyethylene	8, 9, 10
10.	Polyoxymethylene/polyamide-6/66	11, 12
11.	Polyamide-6/polyethylene	13
12.	Polystyrene/polyethylene	14
13.	Polycarbonate/tetramethylene polycarbonate	15
14.	Linear low density polyethylene/low density polyethylene	5
II Negative Deviating Blends (NDB)		
II A Miscible blends		
15.	Polyethyleneoxide/polymethylmethacrylate	16
II B Immiscible blends		
16.	High density polyethylene/polyamide-6	17
17.	Polystyrene/polyethylene	18, 19
18.	Polystyrene/polypropylene	18, 19
19.	Polystyrene/polymethylmethacrylate	20
20.	Polyoxymethylene/poly(ethylene-co-vinylacetate)	21
21.	Polyethyleneterephthalate/polyamide-6	22
22.	Polystyrene/polyoxymethylene	23
23.	Polymethylmethacrylate/polyamide-12	24
24.	Low density polyethylene/polyoxymethylene	24, 25
25.	Polystyrene/polycarbonate	24, 25

No.	Blend
III Po	
26.	Polycarbonate
27.	Polybutadiene
28.	Low density
29.	Cellulose
30.	Polyoxyethylene
31.	High density
32.	Low density
33.	Polymethylmethacrylate
34.	Polyethylene

References: 1. W. 1978; 4. T. U. 1978; 7. T. Fujimura et al. 1981; 10. D. Curto et al. 1981; 17. K. C. D. Han, 1984; 22. Lipatov et al., 1979a; 28. A. N. 1978; Yu. S. Lipatov et al., 1982; 33. L. A. 1982.

The number reported for polyoxymethylene/polyethylene (Wu, 1987) as negative deviation. Judging from PDB, expected to associate.

$$G^0 =$$

where M_{e12} is the experimental methymethacrylate mechanism should be the reduce it. The non-interactive

$$G_N^0 =$$

Since $G_1^0 =$ the M_{e12} in the derived from the macromolecular system involving (3.150) predicts blends is expected

2.7 Interphase, Diffusion and Compatibility 127

Ref.	
5	adiene-b-1,4
6	di-block polymers
7	ate-s-dimethyl siloxane)
8	multiblocks
9	action
10	cation
11	nide-ester exchange
12	ring extrusion
13	logy
14	logy
15	
16	on of oriented fibers
17	on of oriented fibers
18	
19	
19	icious
20	
21	actions
22	actions between SO ₃ H groups in hard segments
23	ic interactions
24	
25	
26	ing nitrile and/or ester ?AE
27	lysis of PVF ₂ / polyviny- lene

et al., 1980; 3. A. Ghaffar et al., 1982; 6. M. A. Harnay and abal et al., 1984; 9. M. Kimura et al. and L. A. Utracki, 1986; 12. L. Z.; 14. J. M. Liegeois and F. Terreur, R. Kamal et al., 1983; 18. M. R. berg et al., 1982; 21. Z.-L. Zhou; 23. A. Eisenberg and M. Hara, 1984; 26. O. Olabisi and A. G.

containing styrene-acrylonitrile copolymer can be successfully analyzed with this approach (Mendelson, 1985; Fowler, 1986; Fowler et al., 1987; Goh et al., 1987; Wu, 1987).

In several commercial polymer blends "modifiers" are used (see Appendix II). The modifier is usually a copolymer containing a rubbery component with interactive one(s). Acrylic-based copolymers, chlorinated polyolefins, ethylene-propylene-diene, poly(ethylene-co-vinylacetate), etc. are frequently used. These play a dual role, compatibilizing and toughening the blend. For this reason they are used at much higher loading than pure compatibilizers; while 1 to 2 wt% of the latter is usually sufficient 20 to 40 wt% of a modifier may be needed (Chuang and Han, 1984; Utracki, 1987, 1988; Hobbs et al., 1988).

Co-reaction of blends to improve the performance has for decades been a practice in the rubber industry (Coran et al., 1985). In high-shear mixers some of the chains in rubbers are broken and re-formed by the free-radical mechanism. A similar phenomenon occurs during intensive mixing of polyolefins. To enhance this process sometimes a source of free radicals, e.g. peroxides, can be added (Paul and Newman, 1978).

Compatibilizations of polyesters and polyamides via an exchange reaction have been reported as well. Transesterification has been used for years to manufacture polyesters (Utracki, 1972) or to modify the properties of miscible polyester blends (Kimura and Porter, 1981; Devaux et al., 1982; Eguizabal et al., 1984; Robeson, 1985; Calahorra et al., 1987). Compatibilization via co-reaction between polyarylate and phenoxy also was reported (Eguizabal et al., 1984). Devaux et al. (1982, 1984) observed that at the initial stage of transesterification between polycarbonate and polybutyleneterephthalate block polymers with reduced solubility are produced. At a later stage, soluble random copolymers are formed. Significant changes of properties on transesterification between polyethyleneterephthalate and polyarylate were reported (Kimura et al., 1983). Particularly interesting is the catalyzed exchange between polyamide-6,6 and polyethyleneterephthalate conducted during a standard processing operation, i.e. extrusion or injection molding (Pillon and Utracki, 1984, 1985, 1986). Due to the small interface area in these immiscible blends, previously the exchange reaction had to be conducted by heating the mixtures for 5 to 30 hours at 220 to 290°C. Use of organic phosphites to enhance coreaction between amine hydroxyl terminated macromolecules (polyamides or polyesters) was reported by Aharoni (1985).

The interpenetrating polymer network, IPN, is a diverse, rapidly developing branch of polymer blends technology. The principle is to combine two polymers into a stable interpenetrating network. At least one of these polymers is synthesized and/or crosslinked in the immediate presence of the other. The crosslinking in thermoplastic IPN can be of a physical nature: hard blocks, ion clusters, crystalline region (Sperling, 1981). Most of the IPN's can be classified as compatibilized, immiscible polymer blends or alloys. Controlling kinetics of phase separation during the formation of the IPN (or the semi-interpenetrating polymer networks, SIN's) provide the method of generation of desired properties (Lipatov et al., 1986). The main disadvantage of IPN's is their non-recyclability.

Single phase IPN are also known. Polymerization of vinyl chloride (VC) in the presence of polyethylacrylate, PEA, resulted in a homogeneous system, whereas the physical blending of polyvinylchloride (PVC) with PEA produce immiscible blends (Walsh and Cheng, 1984). Similarly, VC was polymerized in the presence of polybutylacrylate (PBA) (Liegeois and Terreur, 1984). In dynamic tests the resulting PVC/PBA blends behaved as a single phase system in spite of the observed microheterogeneity (standard blends of these two polymers are immiscible).

Crosslinking via irradiation of e.g. low density polyethylene/polypropylene blends (Rizzo et al., 1983; Brooks, 1983) follows on earlier works where vulcanization has been used to stabilize polymer blends (e.g. Kuleznev et al., 1975). Irradiative crosslinking is a free radical process resulting in a similar structure to that created by chemical crosslinking or vulcanization (Nakamura et al., 1987). The aim of the process is first to generate the compatibilizing

1.3 Fundamental Principles for Development of Polymer Alloys and Blends 23

presence of the other polymer, e.g. blends with high initial modulus and high yield strength may at the same time show large values of the maximum strain at break (*Inoue et al.*, 1984, 1985, 1987).

An important part of the thermodynamics of PAB's deals with properties of the interphase. In a simple approach, addition of the third ingredient is similarly treated as that of surfactant to oil/water mixture. Since the equilibrium thermodynamics considers neither dynamics of dispersion nor size of the phases, the way one may estimate the compatibilizer effect is to assume its crosssectional area at the interphase and then compute the total interface area. It is not surprising that for polymeric compatibilizers the method rarely works. There are several reasons for this: polydispersity of all three ingredients affects the miscibility of the compatibilizer, its micellization is frequently observed inside one of the phases, and the rate of equilibration is very slow in comparison to that of the low molecular weight surfactant. The theory which provides good description of compatibilization using diblock copolymers is that developed by Noolandi and his collaborators (Part 2.3.7); it predicts the degree of dispersion, thickness of the interphase as well as the interfacial tension coefficient. Examples of compatibilized systems are listed in Table 2.16 (p. 125).

The thermodynamics of polymer blends leads one to expect two types of morphology. The first originates in the dynamics of phase separation and exists for a short time before phase ripening takes over (see Part 2.4). The second type of morphology is controlled by the equilibrium thermodynamics where the size and shape of the phase is determined by minimization of the total free energy of the system, including that of the interface.

1.3.2 Flow and Flow-Induced Morphology

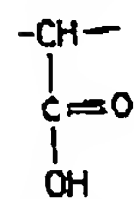
The Part 3 starts with a brief summary of the experimental rheology then reviews the flow behavior of the PAB model systems. It is of utmost importance to map-out the known behavior of diverse liquid systems, to recognize the established principles behind correlations in classical multiphase rheology, before moving on to the unknown territory of PAB's. It is useful to recapitulate what has been learned over the years from those systems that may be considered PAB models.

Excellent models of the miscible blends are solvent mixtures or blends of polymeric fractions (homologous polymer blends). For immiscible blends with low viscosity of the dispersed phase the emulsions or foams, for those with high viscosity the suspensions can be used as model. Furthermore, the flow of compatibilized blends is well simulated by that of block copolymers.

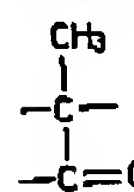
In the single phase binary mixtures, the thermodynamics plays an important role. Both, the free volume additivity in non-interacting system, and the energetic interaction parameters in others similarly affect the viscosity-composition, $\eta-\phi$, dependence generating slightly higher viscosities than those predicted by the simple log-additivity rule (see Part 3.2.1).

The emulsion and suspension flows both suggest that the viscosity must increase with the volume fraction of the dispersed phase. Since in blends, at the two ends of the concentration scale, the roles of dispersed/matrix polymer are reversed, the simplest emulsion model lead one to expect that for PAB, $\eta-\phi$ dependence will show a positive deviation from the log-additivity rule (or PDB for short). On the other hand *Lees'* (1900) model of additivity of components' fluidity, as well as the one proposed by *Lin* (1979) for telescopic flow of liquid mixtures, lead one to expect negative deviation from the log-additivity rule (or NDB behavior). This type of flow has been frequently observed in antagonistically immiscible polymer blends. In capillary flow the slip surfaces are most often concentric, created within the cylindrical volume of the low viscosity phase.

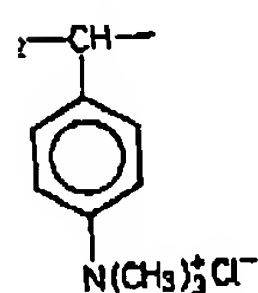
d. PAA



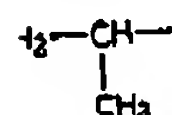
/lic acid, PMA



methyltrimethyl ammonium



endc, PP



adiene-co-acrylonitrile) with 30
acrylonitrile content.
ylene-co-vinyl acetate) with 60
vinyl acetate content.

mer-polymer miscibility is not
or to devise methods for blend
lus, HDT, etc. The miscibility
her types of compatibilization

ccessible range of variables, e.g.
ng with a particular attention to
quenching" (see Part 2.4.2) can
ture even at a concentration of
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onent nearly unaffected by the

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